III. "Notes of Researches on the Poly-Ammonias."—No. VI. New Derivatives of Phenylamine and Ethylamine. By A. W. Hofmann. Received June 9th, 1859.

Some time ago* I communicated to the Royal Society some results obtained in studying the action of dibromide of ethylene upon phenylamine. The principal product of this reaction was found to be a well-defined crystalline compound with basic characters. By the analysis of the base itself, and of several of its combinations, it had been proved that the formula

$$C_{16}H_9N=\left.\begin{matrix}(C_4H_4)''\\C_{12}H_5\end{matrix}\right\}N$$

is the simplest atomic expression for the new substance; but the action of iodide of methyl and of ethyl upon this body having given rise to compounds

$$C_{34}H_{21}N_2I=\left.\begin{matrix}C_{16}H_9N\\C_{16}H_9N\end{matrix}\right\}C_2H_3I$$

and

$$C_{36}H_{23}N_2I=\left.\begin{matrix}C_{16}H_9N\\C_{16}H_9N\end{matrix}\right\}C_4H_5I,$$

I was induced to assume the formula

$$C_{32}H_{18}N_2=\left.\begin{matrix}(C_4H_4)''\\(C_{12}H_5)_2\end{matrix}\right\}N_2$$

as representing the true constitution of the basic body, which thus appears as a diammonia, in which 2 equivs. of hydrogen are replaced by 2 equivs. of phenyl, and 4 equivs. of hydrogen by 2 molecules of diatomic ethylene.

This view involves the existence of a basic compound,

$$C_{28}H_{16}N_2=\left.\begin{matrix}(C_4H_4)''\\(C_{12}H_5)_2\\H_2\end{matrix}\right\}N_2,$$

i.e. of a diphenyl-diamine in which only one molecule of diatomic ethylene has been substituted for hydrogen.

Experiment has not failed to realize the body pointed out by theory. A mixture of dibromide of ethylene with a large excess of phenylamine (1 vol. of dibromide of ethylene and 4 vols. of phenylamine) rapidly solidifies to a crystalline mass. Treatment with

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water removes from this mixture a very considerable proportion of hydrochlorate of phenylamine, leaving a brown resinous substance, which gradually but imperfectly solidifies. This substance forms a hydrochlorate which is difficultly soluble in concentrated hydrochloric acid, and which may be readily purified by repeated crystallizations from boiling alcohol. The pure hydrochlorate dissolved in water, and mixed with potassa or ammonia, furnishes the free base, which generally separates as an oil, rapidly solidifying into a crystalline substance. This may be further purified by repeated crystallizations from diluted alcohol.

Analysis, in fact, assigns to this body the formula

$$C_{28}H_{16}N_2 = \left.\begin{matrix}(C_4H_4)''\\(C_{12}H_5)_2\\H_2\end{matrix}\right\}N_2,$$

which was confirmed by the analysis of the dichloride—

$$\left[\left.\begin{matrix}(C_4H_4)''\\(C_{12}H_5)_2\\H_4\end{matrix}\right\}N_2\right]''Cl_2,$$

and of the platinum-salt—

$$\left[\left.\begin{matrix}(C_4H_4)''\\(C_{12}H_5)_2\\H_4\end{matrix}\right\}N_2\right]''Cl_2,\ 2PtCl_2.$$

The formation of the new body is obvious:

$$4\left[\left.\begin{matrix}C_{12}H_5\\H_2\end{matrix}\right\}N\right] + (C_4H_4)''Br_2 = \left.\begin{matrix}(C_4H_4)''\\(C_{12}H_5)_2\\H_2\end{matrix}\right\}N_2 + 2\left(\left[\left.\begin{matrix}C_{12}H_5\\H_3\end{matrix}\right\}N\right]Br\right).$$

Phenylamine. — Dibromide of Ethylene. — Ethylene-diphenyl-diamine. — Bromide of Phenyl-ammonium.

This substance differs in its physical characters essentially from the base containing 2 molecules of ethylene. The former is very soluble in alcohol and ether, the latter being very difficultly soluble; its fusing-point is 59°, the fusing-point of the latter being 157°.

In order finally to establish the relation between the body which forms the subject of this note and the base previously described, it remained to prove experimentally that the former, when submitted to the action of dibromide of ethylene, may be readily converted into the latter. Nothing is easier than to accomplish this transformation, which, in the presence of alcohol, is rapidly effected at the temperature of boiling water.

Treatment of the product of digestion with water removes the dichloride of ethylene-diphenyl-diammonium, the diethylene-diphenylamine remaining dissolved in the excess of dibromide of ethylene, from which it may be readily extracted by hydrochloric acid.

Preparation of the substance in a state of purity, and comparison of its properties with those of the body previously obtained, established beyond a doubt the transformation, which resolves itself into a simple process of substitution—

$$2\left[\begin{matrix}(C_4H_4)''\\(C_{12}H_5)_2\\H_2\end{matrix}\right\}N_2\Bigg] + (C_4H_4)''Br_2 = \left.\begin{matrix}(C_4H_4)_2''\\(C_{12}H_5)_2\end{matrix}\right\}N_2 + \left[\begin{matrix}(C_4H_4)''\\(C_{12}H_5)_2\\H_4\end{matrix}\right\}N_2\Bigg]''Br_2.$$

Ethylene-diphenyl-diamine being a secondary diamine, it was not without interest to replace the two remaining hydrogen-equivalents by two monatomic molecules. On digesting the base with iodide of ethyl some hours at a temperature of 100°, a beautiful iodide was obtained, crystallizing in well-defined prisms, difficultly soluble in water, but more soluble in alcohol.

This substance contains

$$C_{36}H_{26}N_2I_2 = \left[\begin{matrix}(C_4H_4)''\\(C_4H_5)_2\\(C_{12}H_5)_2\\H_2\end{matrix}\right\}N_2\Bigg]''I_2.$$

Treatment with potassa separates from this iodide the base as a crystalline body fusing at 70°, and resembling in many respects the previous base. It contains

$$C_{36}H_{24}N_2 = \left.\begin{matrix}(C_4H_4)''\\(C_4H_5)_2\\(C_{12}H_5)_2\end{matrix}\right\}N_2,$$

and forms a beautiful platinum-salt crystallizing in needles of the formula

$$[C_{36}H_{26}N_2]''Cl_2, 2PtCl_2.$$

The deportment of phenylamine under the influence of dibromide of ethylene gives a fair illustration of the nature of the substances which are generated, under the influence of diatomic molecules, from primary aromatic monamines.

To complete the study of this subject, I have examined, moreover, the action of dibromide of ethylene upon ethylamine, as a representative of the monamines containing an ordinary alcohol-radical.

Dibromide of ethylene acts upon ethylamine even in the cold, the products of the reaction varying according to the relative proportions of the two bodies, and according to the temperature. Among other products invariably occur the two bromides corresponding to the two salts of the phenyl-compounds mentioned in the previous paragraphs.

These substances are the

Dibromide of ethylene-diethyl-diammonium, $C_{12}H_{18}N_2Br_2 = \left[\begin{matrix}(C_4H_4)'' \\ (C_4H_5)_2 \\ H_4\end{matrix}\right\}N_2\Big]''Br_2$, and

Dibromide of diethylene-diethyl-diammonium, $C_{16}H_{22}N_2Br_2 = \left[\begin{matrix}(C_4H_4)_2'' \\ (C_4H_5)_2 \\ H_2\end{matrix}\right\}N_2\Big]''Br_2$.

I have fixed the composition of the former compound by the analysis of the dibromide of the dichloride and of the base itself, all of which are remarkably well-defined crystalline bodies, and that of the latter by the examination of a well-defined platinum-salt.

The first base, separated by the action of anhydrous baryta from the dry bromide, distils as an oily liquid of a powerfully ammoniacal odour, which solidifies into a brittle crystalline mass not unlike fused stearic acid. The composition of the body is remarkable. It contains

$$C_{12}H_{18}N_2O_2 = \left[\begin{matrix}(C_4H_4)'' \\ (C_4H_5)_2 \\ H_4\end{matrix}\right\}N_2\Big]''O_2,$$

and thus constitutes the dioxide of the diatomic metal, ethylene-diethyl-diammonium.

The second base is liquid, and boils at 185°. It is easily obtained from the dibromide, which, being extremely soluble, may be readily separated from the bromide of the first body. I have experimentally established that this body may be readily procured by the action of dibromide of ethylene upon the dioxide previously mentioned.

The dioxide,

$$C_{12}H_{18}N_2O_2,$$

presents considerable interest in a theoretical point of view. I have determined the vapour-density of this compound by Gay-Lussac's process. Experiment gave the number 2·26. Assuming that the molecule of the body under examination corresponds to 4 volumes of vapour, the theoretical density is 4·62.

The extraordinary discrepancy between theory and experiment may be removed in two ways: viz. either by halving the formula, or by assuming that the molecule of the dioxide of ethylene-diethyl-diammonium corresponds to 8 volumes of vapour, in either of which cases the theoretical density becomes 2·31, closely agreeing with the experimental number 2·26.

I shall discuss the vapour-densities of the diammonias somewhat more fully in a future communication; but I cannot refrain from pointing out even now, that, by dividing the formula by 2, we arrive at an expression containing 1 equiv. of oxygen (O=8), which, in the eyes of those who consider the number 16 as the true molecular value of oxygen, must appear perfectly inadmissible.

IV. "On the Behaviour of the Aldehydes with Acids." By A. GEUTHER, Esq., and R. CARTMELL, Esq. Communicated by Dr. FRANKLAND. Received June 8th, 1859.

[Abstract.]

The authors of this paper, with a view of obtaining a series of combinations homologous with those already obtained from glycol by Wurz—viz. diacetate of glycol, $\left.\begin{matrix} C_4H_4 \\ C_4H_3O_2 \\ C_4H_3O_2 \end{matrix}\right\} O_4$, and the isomeric body of Geuther from common aldehyde, by the action of anhydrous acetic acid,—have subjected common aldehyde, acrolein, and oil of bitter almonds to the action of hydrochloric, hydriodic, and sulphurous acids.

I. *Acrolein,—Metacrolein.*

1. *Acrolein and Hydrochloric Acid.*

By acting on acrolein, $C_6H_4O_2$, with dry hydrochloric acid gas, a body is formed of the composition $C_6H_5O_2Cl$, resulting from a direct combination of one atom of aldehyde with one atom of the acid. This substance is insoluble in water, and can be washed with it in order to free it from any excess of acid or acrolein which may be still present. By drying, which can only be done over sulphuric acid at low temperatures, the body, for which the authors propose the name of hydrochlorate of acrolein, is obtained in a mass of white crystals, presenting a texture like that of velvet. It melts at 32° C. into a thick oil, having a smell of slightly rancid fat. It is